Thin Films and Surface Modification
Room Naupaka Salon 5 - Session TF2-TuE

Thin Films - Processing

Moderator: Christopher Muratore, University of Dayton

7:40pm **TF2-TuE-7 Guided Combinatorial Synthesis, High-Throughput Materials Characterization and Machine Learning Methods Expedite the Discovery of Improved Pt-Au Thin Films***, **David Adams**, T. Shilt, R. Kothari, K. Dorman, C. Martinez, C. Sobczak, S. Addamane, M. Jain, F. DelRio, M. Rodriguez, B. Boyce, R. Dingreville,* Sandia National Laboratories

Sputter-deposited Pt-Au thin films have been reported to develop a stable, nanocrystalline structure that exhibits high hardness and exceptional resistance to fatigue damage, yet little is known about how these characteristics vary with PtxAu1-x composition and processconditions. Toward this end, we describe an extensive combinatorial Pt-Au thin film library

which spans large ranges of binary stoichiometry and deposition atomistics.

Our approach to combinatorial material synthesis implements confocal magnetron sputtering of two elemental sputter targets. Kinematic Monte Carlo SIMTRA simulations helped guide efficient experiments that achieved a broad range of composition of PtxAu1-x (from x ~ 0.02 to0.93) in relatively few (i.e., 3) depositions. The produced films were subsequently characterized using high-throughput, ex-situ methods to further accelerate materials discovery. Automated nano-indentation, X-ray reflectivity, X-ray diffraction, Atomic Force Microscopy, surface profilometry, four-point probe sheet resistance techniques, and Wavelength Dispersive Spectroscopy determined how hardness, modulus, density, surface roughness, structure, and

resistivity vary with film stoichiometry and process parameters.

Combinatorial Pt-Au films displayed an assortment of properties with the hardness of some films exceeding values reported previously for this material system. High hardness, high modulus, and low resistivity were generally attained when using increased deposition energy and reduced angle-of-incidence processes. Finally, we discuss a machine learning approach trained on this complex combinatorial space, which offers new insights into our understanding of these films. An unsupervised clustering algorithm based on variational inference was implemented to encode the different modalities into a shared latent representation. Through analysis of this representation, we identified distinct mechanistic regimes with correlations across modalities. Overall, these efforts help pinpoint promising, new PtxAu1-x compositions for

future study and reveal strategies for improved deposition.

Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. SAND2024-10392A

8:00pm **TF2-TuE-8 Dynamic Fracture of Copper/silica interfaces***, **Cristian Ciobanu**,* Colorado School of Mines and NIST*; F. Bobaru,* University of Nebraska-Lincoln, USA*; G. Stan,* National Institute of Standard and Technology, Gaithersburg, Maryland 20899 USA

Within the real of recent efforts to address new challenges in semiconductor packaging, the hybrid bonding between a dielectric (e.g. silica) and a metal (usually copper) occupies a special place. This direct bond interconnect holds the key to superior functionality, high-density packaging, and low-power operation of future semiconductor devices. However, as the dimensions of the copper interconnects decrease, preparing high quality hybrid bonding that withstands further processing or packaging becomes a challenge. At micron or submicron dimensions, the copper pads or bumps may debond from the silica matrix, which can compromise at least the mechanical integrity of the packaging. In this work, we present a study of dynamic fracture in a heterogeneous system consisting of a copper pad embedded in a silica matrix using peridynamics simulations based on the Fast Convolution-Based Method (FCBM) for spatial discretization and an explicit time marching scheme. Depending on the interface bonding energy, we show different cracking scenarios encountered when a crack initiated in the matrix propagates towards and through the metal inclusion. Crack propagation around the inclusion is consistent with low bonding energy, and we use the simulations to map out the acceptable bonding ranges for different loadings, i.e. those for which cracks propagate through (rather than around) the interface. These results may provide guidance in understanding the cracking of single or multiple pads, and can help estimate acceptable ranges of bonding energy, pad dimensions, and packing density (pads per area).

8:20pm **TF2-TuE-9 Maskless Localized Atomic Layer Deposition Applied to Surface Functionalization***, T. Souvignet, J. Carlotti, V. Salles, M. Maillard, **Catherine Marichy**,* Laboratoire des Multimatériaux et Interfaces - Universite Claude Bernard Lyon 1, France

Nowadays, interest in surface engineering is strongly expanded in many domains like nanoelectronics, energy, transportation, medicine, and the environment. Especially, precise (micro-) surface functionalization patterning are sought after for many devices and applications such as self-cleaning surfaces, microfluidic devices, moisture harvesting and anti-fogging coatings as well as bio-sensor, bio-microarray, and efficient water management in fuel cell.

Maskless fabrication approaches are highly attractive as they enable rapid prototyping of surface functionalities. Based on self-limiting surface reactions, Spatial Atomic Layer Deposition (SALD) technique has recently enabled localized deposition with a control of the film thickness at the atomic scale.[*1–4*]

Using a modified open-air SALD head, we successfully demonstrated the maskless deposition of uniform and homogenous oxide thin films with a lateral resolution tuned from millimeters to hundred micrometers range while keeping a film thickness in the range of a few to hundreds of nanometers with a control at the nanoscale.[*4*]

Herein, surface functionalization using of this maskless SALD approach is introduced. From alkyl silane, it is indeed possible to locally modify the surface properties (hydrophilic/hydrophobic character, etc.) by grafting monolayers, without change of surface topography. Tuning the functionalization degree/saturation of the grafting sites is achieved to modulate the hydrophobic character of the patterns. Contact angles and surface energies are determined before and after functionalization. On patterns, gradient of composition occurs that induces a controllable gradient of hydrophobicity, as demonstrated by the presence of a wetting hysteresis. Imprinted gradients in wettability are particularly interesting for controlling the dropwise condensation of vapor and drop displacement.

1. C. A. Masse de la Huerta *et al.*, *Advanced Materials Technologies*. **5**, 2000657 (2020).
1. P. Poodt, B. Kniknie, A. Branca, H. Winands, F. Roozeboom, *physica status solidi (RRL) – Rapid Research Letters*. **5**, 165–167 (2011).
1. M. Aghaee, J. Verheyen, A. A. E. Stevens, W. M. M. Kessels, M. Creatore, *Plasma Processes and Polymers*. **16**, 1900127 (2019).
1. L. Midani, W. Ben-Yahia, V. Salles, C. Marichy, *ACS Appl. Nano Mater.* **4**, 11980–11988 (2021).

8:40pm **TF2-TuE-10 Advanced Atomic Level Patterning Process by Area Selective Atomic Layer Deposition Integrating Atomic Layer Etching***, **Seo-Hyun Lee**, J. Lee, J. Oh, W. Kim,* Hanyang University, Korea

As semiconductor devices continue to be miniaturized, the reduction in the width of their components has become significant, prompting increased research into 3D structured patterns. Traditional optical lithography-based patterning methods, though commonly utilized, face challenges such as complex processing steps, escalating costs, and difficulties in achieving patterns below 10 nm. To overcome these limitations, we have explored the use of area-selective atomic layer deposition (AS-ALD), a bottom-up thin film deposition technique, which enables selective growth of thin films in specified regions. A malonate-based inhibitor was introduced in the gas phase to deactivate non-growth regions, *i.e.*, SiN substrates, allowing SiO_2 thin films to grow selectively via ALD only on growth regions, *i.e.*, SiO_2 substrates. However, the AS-ALD process often results in unintended deposition of ALD films in non-growth regions, thereby compromising the selectivity between growth and non-growth regions. To address this issue, a post-etching process using atomic layer etching (ALE) was implemented to remove the undesired SiO_2 films deposited on the SiN substrates. Through a repeated sequence of inhibitor exposure, SiO_2 film deposition, and post-etching, we precisely achieved deposition selectivity of 10 nm-thick SiO_2 films, confined exclusively to the SiO_2 substrates.Furthermore, this deposition selectivity was also achieved when applying the sequences to a patterned SiO_2/SiN substrate, demonstrating its suitability for versatile use in upcoming semiconductor devices. This methodology can be leveraged for application in 3D NAND fabrication processes, particularly utilizing the results obtained on SiO_2 and SiN substrates.

Author Index

Bold page numbers indicate presenter